Coulostatic Method for Rapid Estimation of Corrosion Rate; Application to SB46 in 1N H₂SO₄ and SS41 in Distilled Water

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A coulostatic method for rapid evaluation of corrosion rates was developed and applied to mild steels in aqueous solutions. In this method, the decay of polarized potential was recorded on open-circuit after applying a small amount of charge. According to the theory developed, polarization resistance, R_p , for SB46 immersed for 2 hours in 1 N H₂SO₄ was estimated to be 7.9 Ωcm^2 . This agrees fairly well with the value of 5.6 Ωcm^2 obtained by polarization curve measurement. The method is also applied to SS41 in distilled water. The R_p values obtained were 2.4 k Ωcm^2 , 2.1 k Ωcm^2 and 1.1 k Ωcm^2 for immersion times of 45, 51 and 74 hours, respectively. These values are similar to the average polarization resistance, 2.2 k Ωcm^2 , or the corrosion rate of 21 mdd obtained from the weight loss measurement at the immersion time of 75 hours. The coulostatic method developed in this study can be applied without ohmic drop correction, even in distilled water and the time needed to complete the measurement is considerably shorter compared to the usual linear polarization method.

1. Introduction

The weight loss measurement has so far been used as the most reliable method for the evaluation of corrosion rate of metals, but it has disadvantages such as time consuming and being difficult to estimate momentary changes in corrosion rate.

For the purpose of selecting suitable materials, development of rapid evaluation methods has strongly been desired. To meet this requirement attempts have been made to develop electrochemical techniques. McDonald and Marsh developed pulse polarizer. With this apparatus they recorded the time-variation of the potential after polarizing a test piece with a relatively large amount of charge.¹⁾ Their method seems to be useful to obtain a qualitative information about metal corrosion, although it is unable to estimate corrosion rate.

The linear polarization method developed by Stern and co-workers²⁻⁴⁾ has widely been applied to obtain corrosion rates.^{5,6)} The method certainly gives reliable results but it has serious disadvantages that it requires ohmic drop correction and takes a long time for measurement.

Delahay^{7,8)} proposed the coulostatic method for the kinetic study of an electrode system containing redox species in solution. In this method a known small amount of charge is supplied to the electrode at equilibrium and the potential decay

curve of the electrode is recorded for analysis.

We attempted to apply the coulostatic technique to the corrosion study and found that the result obtained in the preliminary measurement was considerably hopeful. In the present paper, we will discuss the applicability of the coulostatic method to a rapid evaluation of corrosion rate of metals from the theoretical point of view, and represent the results obtained with SB46 in 1 N H₂SO₄ and SS41 in distilled water.

2. Theoretical

When a small amount of charge is applied as a pulse to a test piece whose potential is kept at first at the corrosion potential E_{corr} , the potential will quickly be changed to some potential E_m . Overpotential of the test electrode, η_0 , immediately after the charging of double layer is

$$\eta_0 = E_m - E_{\text{corr}} \quad (1)$$

After cutting the current, the potential tends to go back to E_{corr} due to the corrosion reaction. If the charge supplied is consumed entirely by the corrosion reaction and that the concentration polarization is negligibly small, the relation between the overpotential η_t and the faradaic current density I_t at time t will be expressed by

$$\begin{aligned} I_t/I_{\text{corr}} = & \exp \{(\alpha_+ \eta_+ F \eta_t)/RT\} \\ & - \exp \{-(\alpha_- n_- F \eta_t)/RT\} \end{aligned} \quad (2)$$

where I_{corr} is the corrosion current density, α_+ and α_- are the transfer coefficients for anodic and cathodic reactions and n_+ and n_- are the numbers

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of electrons involved in the anodic and cathodic reactions, respectively. R , T and F have the conventional physical meaning. When the absolute value of η_i is less than a few millivolts, Eq. (2) can be simplified to the following Stern-Geary equation²⁻⁴⁾

$$I_t = 2.3 I_{\text{corr}} \{ (\beta_a + \beta_c) / \beta_a \beta_c \} \eta_t \quad (3)$$

where

$$\beta_a = 2.3 RT / (n_+ \alpha_+ F), \quad \beta_c = 2.3 RT / (n_- \alpha_- F).$$

Assuming that the double layer capacity per unit area C_d is constant within a small potential fluctuation, we can write Δq , the amount of charge density consumed by the corrosion reaction from time 0 to t , as

$$\Delta q = C_d (\eta_0 - \eta_t). \quad (4)$$

From Eq. (3), Δq is also expressed as

$$\Delta q = \int_0^t I_t dt = \int_0^t 2.3 \{ (\beta_a + \beta_c) / \beta_a \beta_c \} \eta_t \cdot I_{\text{corr}} dt. \quad (5)$$

Combining Eqs. (4) and (5), we obtain

$$-C_d d\eta_t / dt = 2.3 \{ (\beta_a + \beta_c) / \beta_a \beta_c \} \eta_t \cdot I_{\text{corr}}. \quad (6)$$

Solving Eq. (6) under the condition that $\eta_t = \eta_0$ at $t=0$, we derive

$$\eta_t = \eta_0 \exp \{ -2.3 I_{\text{corr}} \cdot t / (C_d K) \} \quad (7)$$

where

$$K = \beta_a \beta_c / (\beta_a + \beta_c).$$

Equation (7) suggests that the overpotential, $\eta(t)$, decays exponentially with time t . Using polarization resistance R_p in place of $K/2.3 I_{\text{corr}}$ ⁸⁾ in Eq. (7), we have

$$\eta_t = \eta_0 \exp \{ -t / (C_d R_p) \}. \quad (8)$$

Polarization resistance R_p in Eq. (8) is one of the most important parameters of corrosion rate. Eq. (8) is rewritten as

$$\log \eta_t = -0.434 t / (C_d R_p) + \log \eta_0. \quad (9)$$

From Eq. (9), the value of η_0 can be obtained by extrapolating $\log \eta_t$ to $t=0$, if $\log \eta_t - t$ plot gives a straight line. Once η_0 is determined, C_d can readily be calculated from

$$\Delta q = C_d \eta_0, \quad (10)$$

where Δq is the amount of charge density applied to the double layer from a capacitor in the equipment. Usually C_d is in the range $10^{-4} \text{ F/cm}^2 \sim 10^{-5} \text{ F/cm}^2$, η_0 being $10 \sim 1 \text{ mV}$ if Δq is $0.1 \mu\text{C/cm}^2$. Using the values of η_0 and C_d thus obtained, we can calculate R_p from the slope of $\log \eta_t - t$ curve (Eq. (9)).

Fig. 1. Circuit of the coulostat: WE, test piece as working electrode; RE, reference electrode; CE, counter electrode; OA, operational amplifier; D, voltage recorder; RL, relay; C_1 , capacitor.

3. Experimental

3.1 Apparatus

The circuit diagram of the coulostat used is shown in Fig. 1. The test piece (working electrode) is set in a electrolysis cell together with counter and reference electrodes. At first, a small capacitor C_1 is charged up to a certain voltage through a potentiometer composed of battery B_1 and variable resistor VR_1 . Then by means of a relay RL , the charge stored in C_1 is applied abruptly to the test piece whose potential is E_{corr} . After that, overpotential-time curve was recorded with Iwasaki SS-5003 synchroscope. OA indicated in Fig. 1 is an operational amplifier used as a voltage follower.

3.2 Electrodes and Electrolytes

Iron test pieces were cut from a) JIS SB46 and b) SS41 coupons, geometric surface area being 9 cm^2 and 5 cm^2 respectively. Before the measurement, they were polished with $0.05 \mu\text{m}$ Al_2O_3 powder and degreased with acetone. Platinum foils of 10 cm^2 plated with platinum black according to Yoshizawa *et al.*⁹⁾, were used as counter and reference electrodes. The potential of the reference electrode was stable enough to measure the potential variation of the test piece for a short time. However, this had to be replaced by a saturated calomel electrode when polarization curve was measured. The electrolytic solution of $1 \text{ N H}_2\text{SO}_4$ was prepared by reagent grade acid and doubly distilled water having conductance less than $1 \times 10^{-6} \Omega/\text{cm}$. All experiments were carried out at room temperature ($28 \pm 1^\circ\text{C}$) under an atmospheric pressure without expelling the dissolved oxygen.

4. Results and Discussion

4.1 SB46 in $1 \text{ N H}_2\text{SO}_4$

The overpotential-time curve ($\eta_t - t$ curve) for SB46 measured in $1 \text{ N H}_2\text{SO}_4$ after 2 hours of im-

Fig. 2. Polarization potential (η_t)–time (t) curve for SB46, obtained in 1 N H_2SO_4 after immersion for 2 hours. Charge applied was $5.82 \mu\text{C}$.

Fig. 3. $\log \eta_t$ – t plot of the curve in Fig. 2.

Fig. 4. Polarization curve for SB46, obtained in 1 N H_2SO_4 after immersion for 2 hours. E and I are the potential of the test piece and the faradaic current density, respectively.

mersion was shown in Fig. 2, the applied charge Δq being $5.82 \mu\text{C}$. Corrosion potential of SB46 just before the charging was -0.50 V vs. SCE. The values of $\log \eta_t$ were plotted against t in Fig. 3, indicating a linear relationship between these quantities. The value of η_0 determined by extrapolating $\log \eta_t$ to $t = 0$ was 3.0 mV . Differential capacity C_d was calculated to be $216 \mu\text{F}/\text{cm}^2$ by the aid of Eq. (10). Polarization resistance R_p thus obtained was $7.9 \Omega \text{cm}^2$. We have also calculated the value of R_p from the polarization curves. The polarization curves measured for the same test piece (Fig. 4) indicate that $I_{\text{corr}} = 2.8 \text{ mA}/\text{cm}^2$, $\beta_a =$

51 mV and $\beta_c = 128 \text{ mV}$. From these parameters R_p is calculated to be $5.6 \Omega \text{cm}^2$ using $R_p = K/2.3 I_{\text{corr}}$. Agreement between the values of R_p obtained with two different methods is satisfactory. It should be noted that the value of C_d obtained is considerably larger than that of a smooth electrode such as mercury drop¹⁰⁾ ($10 \sim 40 \mu\text{F}/\text{cm}^2$), suggesting an increased surface roughness of the test piece due to corrosion.

4.2 SS41 in distilled water

The overpotential-time curves for SS41 in distilled water were also measured at various immersion times. As an example, Fig. 5 shows the relation between $\log \eta_t$ and t obtained after the immersion time of 45 hours. As can be seen, the $\log \eta_t$ vs. t relation does not fall on a straight line at the initial stage but it becomes linear after 200 ms. The initial deviation can be ascribed to the poor conductivity of distilled water, where a longer time was required to charge the double layer. In other words, the charging process still continued to occur during the potential decay in the initial stage, and the ohmic drop effect due to the charging current is considered to overlap to the overpotential. This was confirmed by using the equivalent circuit (Fig. 6) corresponding to the corrosion cell system, where resistors, R_s' , R_p' and capacitor C_d' were regarded as solution resistance, polarization resistance and double layer capacitance, respectively.

Fig. 5. $\log \eta_t$ – t relationship for SS41 in distilled water measured after immersion for 45 hours. Charge applied was $1.83 \mu\text{C}$.

Fig. 6. Equivalent circuit for the test cell. R_s' , R_p' and C_d' correspond to solution resistance, polarization resistance and double layer capacitance, respectively.

Fig. 7 Log E_t - t relationship for the equivalent circuit. (a) $R_s'=97.7\text{ k}\Omega$, $R_p'=29.5\text{ k}\Omega$, $C_d'=9.87\text{ }\mu\text{F}$; (b) $R_s'=0\text{ }\Omega$, $R_p'=29.5\text{ k}\Omega$, $C_d'=9.87\text{ }\mu\text{F}$. For both cases, charge applied was $0.370\text{ }\mu\text{C}$. E_t is the terminal voltage between a and b in Fig. 6.

Table 1. Double layer capacity and polarization resistance of SS41 in distilled water for various immersion time $\bar{t}$.

$\bar{t}$, hr	Δq , C/cm ²	η_0 , mV	C_d , $\mu\text{F}/\text{cm}^2$	R_p , $\text{k}\Omega/\text{cm}^2$
45	0.366	2.16	169	2.4
51	0.364	1.83	199	2.1
74	0.376	1.57	239	1.1

sistance and double layer capacity, respectively. When $R_s'=97.7\text{ k}\Omega$, $R_p'=29.5\text{ k}\Omega$ and $C_d'=9.87\text{ }\mu\text{F}$ a potential decay curve similar to that shown in Fig. 5 is obtained (Fig. 7 curve a). It is also recognized that the deviation in the initial stage disappeared when R_s' was decreased to zero (Fig. 7 curve b). Extrapolation of the linear parts of the logarithmic plots to $t=0$ gave a voltage value nearly equal to that obtained in the case of $R_s'=0$. This voltage corresponds to the over-potential η_0 of the corrosion system in question.

Thus, for 45 hours of immersion, the value of η_0 was determined to be 2.2 mV by extrapolation from the linear parts of the potential-time curve shown in Fig. 6. From the values of η_0 measured at various immersion times C_d and R_p were calculated and tabulated in Table 1.

Now, from the weight loss measurement of the same test piece after 75 hours of immersion, the average corrosion rate V is estimated to be 21 mdd. V can be correlated with R_p using the following equations.

$$V=(M/nF)I_{\text{corr}} \quad (11)$$

$$R_p=K'/I_{\text{corr}} \quad (12)$$

where M is the atomic weight of iron and $K'= \beta_a\beta_c/2.3(\beta_a+\beta_c)$. The constant K' has been determined to be 0.018 in our laboratory by the

galvanostatic linear polarization method and weight loss measurements. Using the above K' value, Tafel slopes were estimated as $\beta_a=70\text{ mV}$ and $\beta_c=105\text{ mV}$. These values are in fairly good agreement with those reported by several authors.¹¹⁻¹³ The R_p value of $2.2\text{ k}\Omega/\text{cm}^2$ thus obtained by the weight loss method is in good agreement with the average of the R_p values tabulated in Table 1. This clearly indicates the usefulness of our coulometric method. The values of C_d given in Table 1 are larger compared to those for a smooth electrode¹⁰, they have a tendency to increase with increasing immersion time. Since C_d is a measure of the surface area, this suggests that the surface roughness of the test piece increases with the time of corrosion.

Another advantage of the present method is that the potential change can be measured without applying current between working and counter electrodes and the method is applicable even to solutions with low conductivity such as distilled water. The coulometric method is a sort of relaxation method, where measurement can be carried out within a very short time.

As described above the coulometric method is quite useful for the evaluation of the instantaneous corrosion rate for SB46 in 1 N H_2SO_4 and SS41 in distilled water. Experiments concerning other metal/solution combinations are in progress.

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